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Published in:
Applied Physics Letters

DOI:
10.1063/1.3495772

Publication date:
2010

Improved thermal stability of gas-phase Mg nanoparticles for hydrogen storage

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(Received 12 August 2010; accepted 10 September 2010; published online 30 September 2010)

This work focuses on improving the thermal stability of Mg nanoparticles (NPs) for use in hydrogen storage. Three ways are investigated that can achieve this goal. (i) Addition of Cu prevents void formation during NP production and reduces the fast evaporation/voiding of Mg during annealing. (ii) Alloying can prevent Mg evaporation: e.g., Mg with Ni forms a thermally stable core/shell ($MgNi_2$/Ni) preventing Mg evaporation during annealing. (iii) Covering Mg NPs with a Ti film leads to suppression of Mg evaporation during vacuum annealing. Indeed, hydrogenation of the Ti/Mg NPs shows formation of the γ-MgH_2 phase as for pure Mg NPs. © *2010 American Institute of Physics*. [doi:10.1063/1.3495772]

Magnesium with its high gravimetric hydrogen storing capacity of 7.6 wt % is considered one of the main candidates for hydrogen storage.[1] Although the improvement in kinetics of hydrogen absorption/desorption has been achieved by ball milling Mg with catalysts and alloying,[2–5] the problem associated with high formation enthalpy of Mg-hydrides has driven attention to nanoengineering. Nanoparticles (NPs) and nanowires of Mg above 50 nm do not show any significant improvement in thermodynamics.[6,7] Similarly, nanoconfinement of Mg-hydride in the porous carbon aerogel scaffold material also did not show any thermodynamic changes.[8–10] On the other hand, theory predictions show that the thermodynamics of MgH_2 can be improved if the size of the NPs can be reduced below 2 nm.[11,12]

Therefore, a lot of interest has been paid to produce Mg NPs below 5 nm, because low desorption temperatures compared to bulk Mg have already been reported.[13,14] However, our recent observations show that a reduction in size will increase the evaporation rate of Mg NPs during annealing in H_2 atmosphere;[15] evaporation even results in the formation of a complete hollow Mg core (Kirkendall effect associated with evaporation). The thermal stability of Mg NPs is a serious issue, because the increase in the vapor pressure with decreasing NP size will always enhance Mg evaporation. Similarly, the voids that are formed during production within Mg NPs (due to oxidation-based Kirkendall effect) have also major impact on accelerating the formation of an empty Mg NP core leaving behind an MgO nanoshell.[15]

These observations show that void formation and increased Mg evaporation rate with decreasing NP size represent formidable limitations for using Mg NPs in hydrogen storage.[15] In this work, we address these problems and discuss strategies to improve the thermal stability of Mg NPs by preventing voiding. These approaches are based on (i) addition of 1/8 Cu to an 7/8 Mg target, (ii) alloying Mg with Ni, (iii) and covering Mg NPs with a Ti film.

The Mg–Cu, Mg, Mg–Ni NPs were produced by an Oxford Applied Research NC200U NP source. The sample chamber was evacuated to a pressure $\sim 1 \times 10^{-8}$ mbar with partial oxygen pressure $\sim 10^{-9}$ mbar.[16,17] Supersaturated metal vapor is produced by magnetron sputtering of a target consisting of Mg(7/8) and Cu(1/8) for Mg–Cu NPs, Mg_2Ni alloy target for Mg–Ni NPs, and pure Mg target for Mg NPs in an Krypton atmosphere (pressure $\sim$0.25 mbar). All tar-

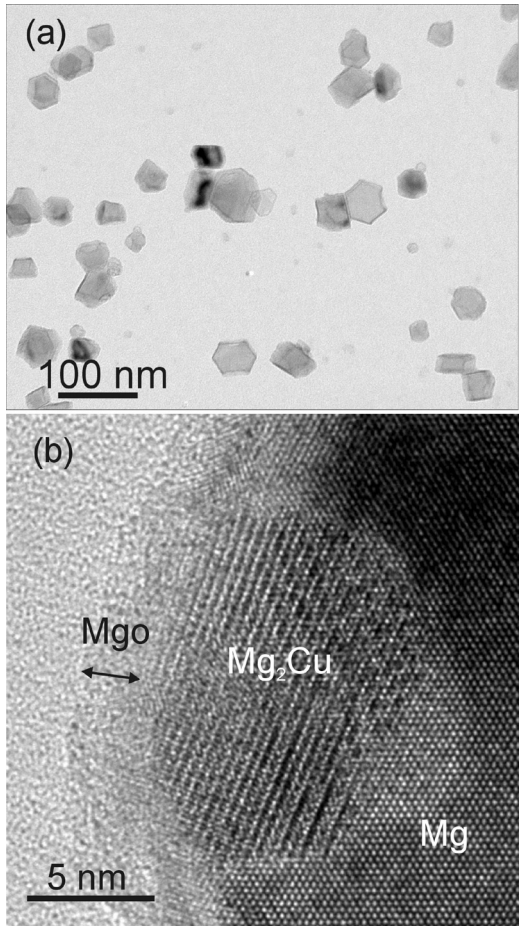

FIG. 1. (a) Bright field TEM image showing an overview of Mg–Cu NPs produced in the size range 15–70 nm without voids. (b) HRTEM image showing an Mg–Cu NP with a Cu rich (Mg_2Cu) part in one of the corners of Mg core, with a very thin amorphous oxide shell exactly where the Cu rich (Mg_2Cu) part is present. In contrast, around the Mg core a crystalline MgO shell is present.

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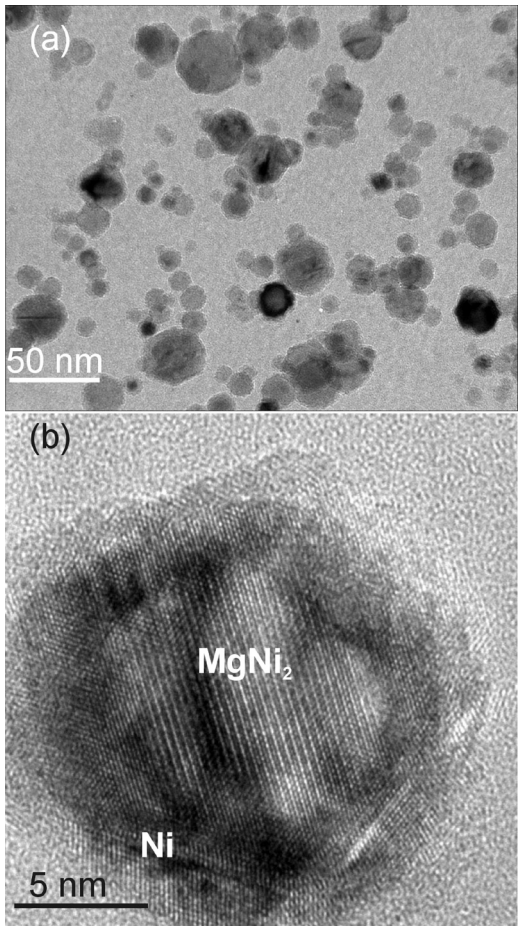

FIG. 2. (a) Bright field TEM image of Mg-Ni NPs after vacuum (*in situ* TEM) annealing at 300 °C for 7 h without any void formation and Mg evaporation. (b) HRTEM image of a core shell $MgNi_2$/Ni NP after annealing at 300 °C for 7 h.

gets were obtained from Alpha Aesar with purity 99.99%. The NPs were deposited on 25 nm thick silicon-nitride membranes, which were used for high resolution transmission electron microscopy (HRTEM) and energy dispersive x-ray (EDX) analysis in a JEOL 2010F TEM. *In situ* covering of Mg NPs with a Ti film of ~15 nm thick was performed with e-beam evaporation, directly after the Mg NPs were deposited on Si-nitride membranes for TEM.[18,16]

During hydrogenation of Mg NPs at 300 °C, a hollow Mg core was formed (due to Kirkendall effect associated with Mg evaporation).[15] Void formation due to metal oxidation is normally known as a Kirkendall effect, because the cation and anion fluxes through the oxide scale are unequal, resulting in a net flow of vacancies, which coalesce into voids below the oxide scale.[18] However, in our case we also associate the Kirkendall effect with evaporation due to the inward diffusion of vacancies (through the oxide) coupled to an outward diffusion of Mg (Ref. 15). The evaporation rate shows a size effect; the smaller the NPs the faster they form an empty Mg core.[15] In controlling the evaporation of Mg and voiding, we started with the addition of Cu to Mg. Figure 1(a) shows that the produced Mg–Cu NPs with an addition of 1/8 Cu to an 7/8 Mg target prevent the void formation in the Mg core. Indeed, the produced Mg–Cu NPs generally have a Cu-rich (Mg_2Cu) part in one of the corners of the Mg core [Fig. 1(b)].

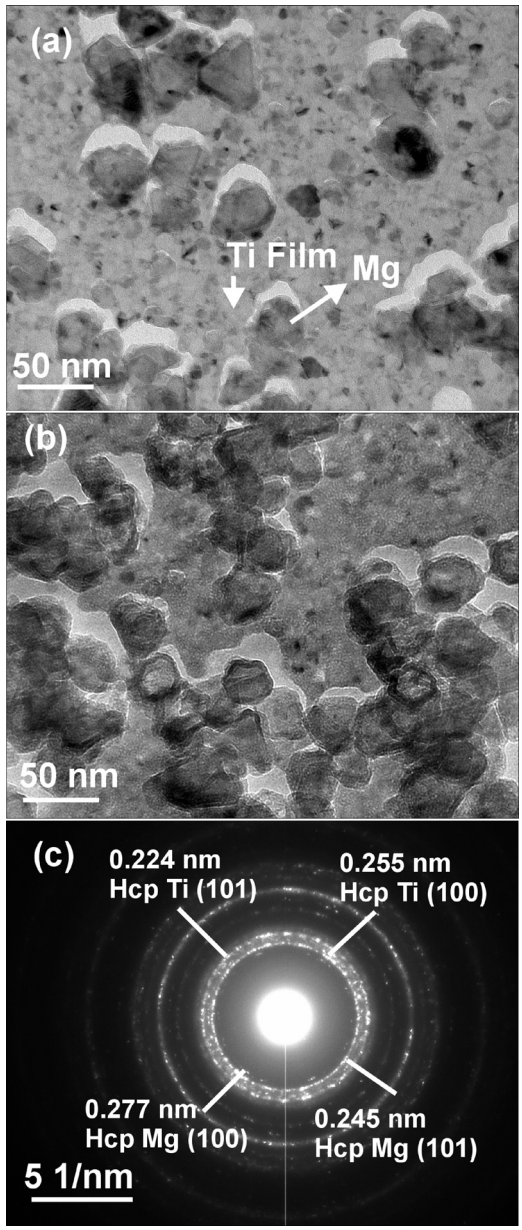

FIG. 3. (a) Bright field TEM image of Mg NPs covered with a Ti film (~15 nm thick). (b) Ti covered Mg NP after annealing in vacuum at 300 °C for 5 h and at 350 °C for 1/2 h without any Mg evaporation and void formation. (c) Diffraction pattern of the sample after annealing showing the presence of Mg, which remains identical to the diffraction pattern of the sample before annealing.

EDX analysis of the Mg–Cu NPs confirmed the presence of Cu in the corners of an otherwise pure Mg core. Furthermore, Fourier transform analyses of the HRTEM images of the Cu rich parts with (interplanar spacing of pure) Mg core as reference confirmed that the Cu rich area is the Mg_2Cu phase. TEM analysis shows that Mg–Cu NPs do not show any hollow faceted voids. These voids were observed in pure Mg NPs at the Mg/MgO interface due to oxidation.[18] The absence of voids in the Mg–Cu NPs can be attributed to the fact that the rate of outward diffusion of the metal (cations) compared to the inward diffusion of oxygen (anions) is reduced. This factor in return indicates that in the Mg core, e.g., outside the Mg_2Cu part, some Cu atoms must have been dissolved in it. Our previous study[15] indicates that the NPs without initial void formation will improve the stability of

the Mg core as compared with Mg NPs with a void.

With the poor thermal stability of Mg NPs during annealing and hydrogenation, it is worth to investigate further alloying effects. Therefore, we produced Mg–Ni NPs, where we varied the composition of Ni in the Mg–Ni NPs, and studied its effect on the thermal stability of Mg. Indeed, we can infer from our TEM analysis that Mg–Ni NPs with on average 60:40 at. % composition are indeed stable after *in situ* TEM annealing, and in hydrogen atmosphere (under 6 bars pressure) held at 300 °C for 40 h without any void formation and evaporation. Figure 2(a) shows bright field image of Mg–Ni NPs after *in situ* TEM annealing at 300 °C for 7 h. Note that the composition of individual NPs can show distinct variations with respect to the 60:40 at. % ratio. Furthermore, the Mg–Ni NPs with $MgNi_2/Ni$ core shell are also stable under *in situ* TEM annealing as it is shown by Fig. 2(b). However, for hydrogen storage it is necessary that the Mg percent is significantly higher in the alloy since it determines the total gravimetric density of hydrogen that can be stored in alloy NPs. Nevertheless, if the Mg content in alloy NPs is increased then also the void formation again develops during annealing of the NPs, although the Mg evaporation was not as serious as it was observed for pure Mg NPs. We also tried to increase the Mg composition with a section target like [(1/4) Ni and (3/4) Mg] but the annealing results show that even though there was a present Ni in the NPs, the evaporation of Mg remained uncontrolled.

With the prospect of hydrogen storage applications, in order to use pure Mg NPs since they have the highest hydrogen gravimetric density (7.6 wt % in bulk), we also considered the case of covering Mg NPs with a nanometer thick (~15–20 nm) Ti layer on top. Although a Ti layer can be used for hydrogen dissociation, and as a catalyst for hydrogen absorption and desorption,[19,20] the main motivation here was to see the effect of Ti in protecting NPs from Mg evaporation.[15] After annealing *in situ* in TEM at 300 °C for 5 h, and 350 °C for 1/2 h (to gauge the temperature effect), Mg NPs covered with Ti remained almost unchanged as Figs. 3(b) and 3(c) indicate. Therefore, Mg NPs covered with Ti favor the suppression of Mg evaporation in comparison with Mg bare NPs. A more detailed discussion will be performed elsewhere. In any case, hydrogenated Mg NPs covered with Ti show the orthorhombic MgH_2 phase along with the TiH_2 phase.

We have shown that the evaporation of Mg NPs depends on their specific situation.[15] The effect of alloying Mg is straightforward, because it reduces the Mg vapor pressure of the alloy with respect to pure Mg. Since the outward Mg flux is reduced also the inward vacancy flux diminishes, and the Kirkendall effect is suppressed. In the case of Ti coverage, the evaporating (pure) Mg NPs quickly attain their equilibrium vapor pressure in the limited volume enclosed by the Ti layer. When this happens no further net evaporation will occur, and the Kirkendall effect is strongly suppressed.

In conclusion, in this work we put emphasis on improving the thermal stability of Mg NPs for possible use in hydrogen storage. Indeed, we have shown that the addition of Cu can prevent the void formation in the Mg NPs during its production. Alloying Mg with Ni can prevent Mg evaporation but it depends on the concentration of Ni in the alloy NPs and requires too much Ni to be of practical use for hydrogen storage. Covering Mg NPs with a Ti film appears highly promising for the suppression of Mg evaporation and the use of Mg NPs for hydrogen storage.

We would like to thank Zernike Institute for Advanced Materials for financial support. We would like to thank J. Th. M. De Hosson for supporting this work.

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